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# REMOVAL OF PHOSPHATE FROM WASTEWATER BY ALUMINUM SALTS WITH SUBSEQUENT ALUMINUM RECOVERY

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The removal of phosphates from wastewaters by aluminum salts such as aluminum sulfate (alum) or sodium aluminate can be accomplished with little difficulty. The removal is accomplished in conventional coagulation and flocculation equipment, followed by clarification. The mechanism of the removal is not thoroughly established. Lea et al (3) have suggested adsorption, but Stumm (8) and Henriksen (2) support the preponderant opinion that the removal is chemical in nature. The following equation expresses the overall reaction for phosphate removal by alum:

$$Al_2(SO_4)_3 + Na_2HPO_4 + 3H_2O \longrightarrow Al(OH)_3 \cdot AlPO_4 \downarrow + Na_2SO_4 + 2H_2SO_4 \quad (1)$$

The stoichiometry is only approximate and is dependent upon *p*H (4).

Although the simplicity of this method of phosphate removal is favorable, the process has serious drawbacks. The cost of the aluminum salts is high, approximately 4¢ per 1,000 gal. of wastewater for removal of 10 mg./liter of phosphorus. Copious quantities of a sludge which dewaters poorly are produced.

Lea, Rohlich, and Katz (3) have experimented with a process which recovers the aluminum from this aluminum hydroxide-phosphate sludge as sodium aluminate and removes the phosphate as a calcium salt. The sludge was dissolved in sodium hydroxide and the phosphate precipitated by addition of calcium chloride. The chemistry of the process is expressed by the following equations:

$$3Al(OH)_3 \cdot AlPO_4 + 15NaOH \longrightarrow 6Na[Al(OH)_4] + 3Na_3PO_4 \quad (2)$$

$$3Na_3PO_4 + NaOH + 5CaCl_2 \longrightarrow \underset{\text{(hydroxyapatite)}}{Ca_5(OH)(PO_4)_3}\downarrow + 10NaCl \quad (3)$$

The exact form of the precipitated phosphate has not been identified. The hydroxyapatite shown in Equation (3) is a probable form. These authors reported that this recovery process reduced substantially the chemical cost of phosphate removal by alum.

Slechta and Culp (6) have reported studies in which the investigations of Lea et al (3) were repeated on a laboratory scale. Their results indicated that the cost of recovered alum was higher than the cost of fresh alum. Part of the discrepancy is due to the fact that Slechta and Culp used lower molar ratios of aluminum to phosphorus, 2 to 1 as compared with 4 to 1. As can be seen from Equations (2) and (3), a higher amount of phosphate per mole of aluminum will substantially increase both the sodium hydroxide and calcium chloride requirement. Slechta and Culp were also discouraged by the fact that mixtures of alum and sodium aluminate were less effective for removing phosphate than alum, indicating that the recovered aluminate from the recovery process would not perform as well as alum.

Slechta and Culp also experimented with a recovery process utilizing only calcium hydroxide for alum recovery. The chemical equation is as follows:

$$3Al(OH)_3 \cdot AlPO_4 + 8Ca(OH)_2 \longrightarrow 3Ca[Al(OH)_4]_2 + Ca_5(OH)(PO_4)_3\downarrow \quad (4)$$

These authors reported a maximum aluminum recovery of 35%. Poor recovery was attributed to precipitation of calcium aluminate. Despite the poor recovery, the chemical cost of recovered alum was less than that of fresh alum. However, when capital and operating costs were included, the cost of recovered alum exceeded the cost of fresh alum.

One recovery route not studied by other investigators is the use of sodium hydroxide-calcium hydroxide mixtures for resolubilizing the aluminum-phosphate sludge. The overall chemical reaction is as follows:

$$3Al(OH)_3 \cdot AlPO_4 + 6NaOH + 5Ca(OH)_2 \longrightarrow 6Na[Al(OH)_4] + Ca_5(OH)(PO_4)_3 \quad (5)$$

It is clear by comparing this equation with Equations (2) and (3) that if this stoichiometry is followed, chemical consumption will be substantially less than for the sodium hydroxide-calcium chloride recovery process.

The purpose of this investigation was to investigate more fully hydroxide processes for recovering aluminum from aluminum-phosphate sludges. In the course of this study, it was found important to investigate the alum

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requirement for phosphate removal and the optimum *p*H conditions for phosphate removal.

## EXPERIMENTAL PROCEDURE

### PHOSPHATE REMOVAL

A standard procedure was utilized in all experiments carried out to determine the relationship between phosphate removal, *p*H, and alum dose. In this procedure, a six-position Phipps-Bird multistirrer* is used with 3-liter beakers. Two liters of wastewater are charged to the beakers, and mixing is started. Aluminum sulfate in solution is added in appropriate amount to each beaker, followed shortly by a predetermined amount of sodium hydroxide to give the desired *p*H. The mixture is stirred at 100 rev./min. for 2 min., followed by stirring at 20 rev./min. for 5 min. The flocculated precipitates which form are allowed to settle for about $\frac{1}{2}$ hr., and samples of supernatant are obtained. The supernatants are filtered through an 0.45-$\mu$ millipore filter. Aluminum is determined by an atomic absorption method, and total phosphorous is determined by standard procedures (7).

### PRODUCTION OF SLUDGE FOR ALUMINUM RECOVERY EXPERIMENTS

The production of sufficient sludge for aluminum recovery experiments requires large volumes of wastewater because alum doses required to remove phosphates are relatively low. To avoid this difficulty, many of the runs were carried out with wastewater which had been enriched in phosphate. For example, if it was desired to carry out sludge treatment at an aluminum concentration of 200 mg./liter and an aluminum/phosphate molar ratio of 2.0, sufficient sodium dihydrogen phosphate was added to the wastewater to build the phosphorous concentration up to 115 mg./liter. Addition of 200 mg./liter of aluminum (added as aluminum-sodium sulfate · 18 water) produced the desired sludge. The flocculation was carried out according to the procedure outlined above, with the *p*H adjusted to an optimum value of 6.2.

This preenrichment procedure suffers from the disadvantage that the sludge is produced in an aqueous solution in which sulfate and sodium ion concentrations are much higher than in the original wastewater. This is the result of the large amount of alum added and subsequent *p*H adjustment by sodium hydroxide. Other tests were conducted without predosing to avoid the difficulty. In this procedure, the alum added is based on the desired aluminum/phosphate ratio in the sludge, and the dose level is calculated from the concentration of phosphate actually in the water. The volume of wastewater is chosen which yields the desired amount of sludge. Large volumes of wastewater are required, and manual coagulating and flocculating procedures are used.

### SOLUBILIZATION EXPERIMENTS

In these experiments, sludge is allowed to settle to a volume slightly less than the volume which gives the desired aluminum concentration for that particular test. Chemicals and distilled water are added to give the desired volume. The beakers (generally 2 or 3 liters capacity) are stirred for specified periods, usually 4 hr., with the Phipps-Bird multistirrer. The beakers are covered to avoid absorption of carbon dioxide from the surroundings.

*Mention of proprietary equipment does not represent endorsement by the Federal Water Pollution Control Administration.

## RESULTS

### ALUM DOSE FOR EFFECTIVE PHOSPHATE REMOVAL

Numerous investigators have studied phosphate removal by alum but have observed widely differing molar capacities (moles phosphorus removed per mole aluminum added) for effective removal. Henriksen (*1*) tabulated the results of a number of studies and found molar capacities ranging from about 0.1 to 0.5. Results are apparently influenced by *p*H and by the type of wastewater. In view of this unsettled picture, experiments were carried out to verify some of the effects, such as the effect of *p*H and effluent, and to estimate the minimum aluminum dosage for effective phosphate removal.

Phosphate removal by alum addition to a synthetic wastewater and to secondary effluent obtained from the activated sludge plant at Lebanon, Ohio, is reported in Figures 1 and 2. Compositions of these and the other wastewaters used in this investigation are reported in Table 1. These data, which were obtained at 25°C., indicate on optimum *p*H of about 6. The optimum is far more marked for the synthetic wastewater than for the actual wastewater. Henriksen (*1*) noted a similar *p*H effect and observed that the optimum *p*H range was shifted to slightly higher values for a real wastewater.

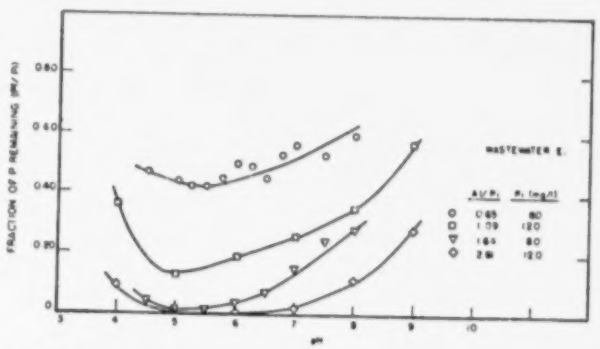


Fig. 1. Effect of *p*H on phosphate removal by alum from a synthetic wastewater.

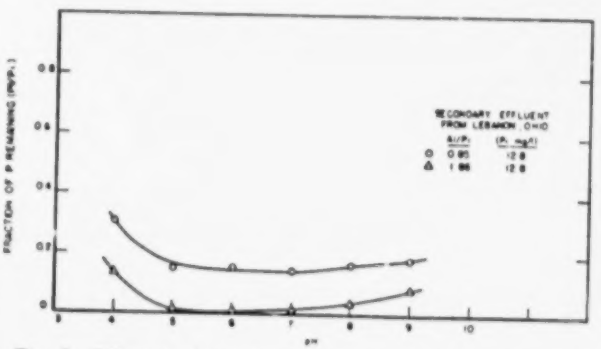


Fig. 2. Effect of *p*H on phosphate removal by alum from an actual wastewater.

TABLE 1. COMPOSITION OF WASTEWATERS USED IN PHOSPHATE REMOVAL AND ALUMINUM RECOVERY TESTS

| Components (mg/l) | $E_1$ (Synthetic) | $E_2$ (Synthetic) | Batavia Al recovery | Lebanon P-removal | Lebanon Al recovery |
|---|---|---|---|---|---|
| Total Phosphorous | varied | 8.4 | 7.0 | 12.8 | 4.6 |
| Aluminum | | | <.05 | | 0.25 |
| Calcium | | 60.0 | 95 | | 120 |
| Magnesium | | 18.4 | 17.7 | | 29 |
| Sodium | 113 | 68.3 | 58 | | 90 |
| Potassium | | 8.2 | 11.6 | | 9.0 |
| Ammonium (as N) | | 13.1 | 15.2 | | 7.0 |
| Bicarbonate | 300 | 148 | 310 | 456 | 464 |
| Chloride | | 133 | 120 | | 159 |
| Sulfate | | 88 | 86 | | 143 |
| Nitrate (as N) | | 6.0 | <0.1 | | <0.1 |
| Total hardness | | | 311 | | 419 |
| pH | | ≈7.5 | 7.6 | | 7.0 |

As noted earlier, Slechta and Culp (6) reported that sodium aluminate-alum mixtures were less effective than alum in removing phosphate. It seems likely that the major portion of this reduced effectiveness was due to the fact that the mixtures high in aluminate produced *p*H values above the optimum. Their phosphate removal data are presented in Figure 3 without regard to the sodium aluminate-alum proportion. The existence of a *p*H optimum is evident. Their data, which were obtained with a soft wastewater, show a narrow effective *p*H range and resemble the results for the synthetic wastewater $E_1$, which had no permanent hardness (Figure 1).

Comparison of the phosphate removal data of various investigators has been made difficult by the lack of a general method of correlation. A general correlation method has resulted by plotting the relative phosphate removal at a given *p*H against the molar ratio of aluminum added to phosphate initially present. This method has been applied to the data obtained on synthetic wastewater (Figure 1) and is presented in Figure 4. For these data, nearly straight lines result; at the optimum *p*H, nearly complete phosphate removal is obtained by a molar ratio of aluminum to phosphate of 1.6. There appears to be no noticeable effect of phosphate concentration on the correlation. Such an effect might be expected in view of the effect of phosphate concentration on the optimum *p*H for turbidity removal noted by Packham (5).

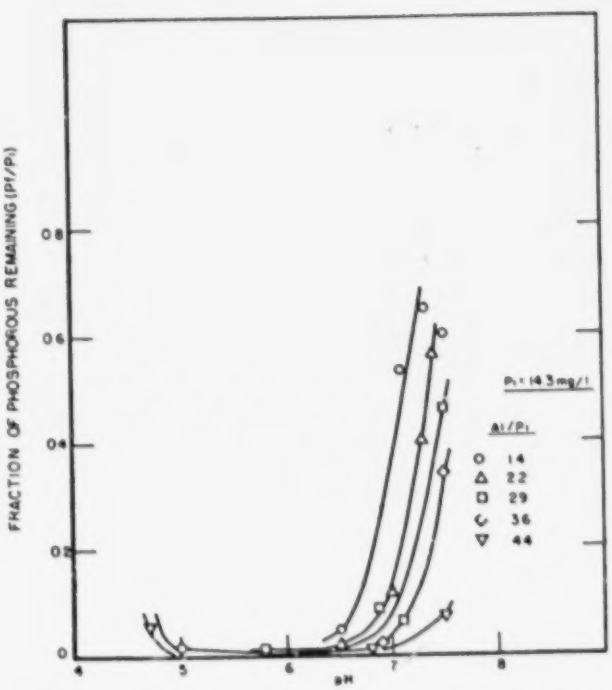


Fig. 3. Slechta and Culp's data on phosphate removal by alum using Lake Tahoe wastewater.

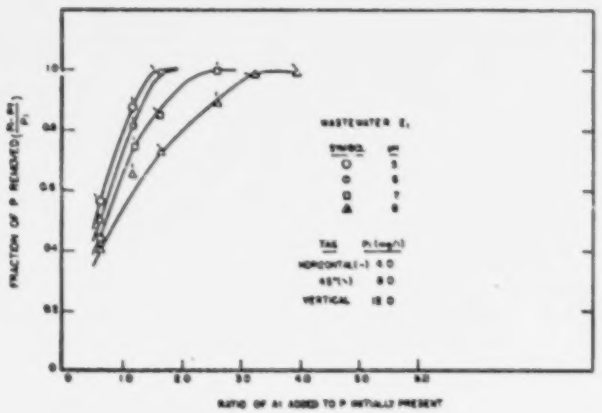

Fig. 4. General correlation of phosphate removal data.

However, Stumm and Morgan (9) indicate that it is the molar ratio of phosphate to aluminum which effects the *p*H optimum for phosphate removal. Thus, as has been observed in Figure 4, the absolute level of phosphate should not be important.

A comparison of data collected by different investigators is shown in Figure 5. The data of Henriksen (*2*) are notable in view of the range of phosphate removals covered and the variation in phosphate level. Curves closest to the ordinate axis show minimum aluminum consumption for phosphate removal. Less than optimum conditions, such as use of a *p*H higher or lower than optimum, or merely decanting the supernatant without filtering, displace the curves in the direction of greater aluminum consumption.

## USE OF CALCIUM HYDROXIDE FOR ALUMINUM RECOVERY

Two sets of experiments were carried out by using calcium hydroxide alone to resolubilize the aluminum in the aluminum hydroxide-phosphate sludge. In the first set of experiments, synthetic wastewaters were used, and in the second set the wastewaters were secondary effluents from municipal plants. Compositions of these wastewaters are given in Table 1.

In the experiments with the synthetic wastewater, aluminum recovery was measured in a half replicate experiment for the following variables and levels: wastewater type ($E_1$ and $E_2$), temperature (25°, 45°C.), form of calcium hydroxide (saturated solution, slurry), dose of calcium hydroxide in moles per mole of aluminum in the sludge (1.0, 1.5, 2.0), and molar ratio of aluminum to phosphate in the sludge (1.8, 2.5). Sludges used were produced by the enrichment technique described above. The experiments were carried out at a total aluminum concentration of 200 mg./liter. This represents a side stream of sludge of slightly less than 10% of the total flow. A side stream of this size is probably close to an upper practical limit for a recovery process.

Analysis of the data obtained in the experiment demonstrated that the calcium hydroxide slurry was not completely dissolving; however, it was possible to correlate the data on the basis of solution *p*H. The data are presented in Figure 6, where percent recovery is shown as a function of *p*H. The percent recovery is actually the ratio of the aluminum in the dissolved state to the total aluminum present. It represents the maximum attainable recovery if all of the dissolved aluminum could be recovered from the sludge which remains after treatment.

The data in Figure 6 for the tests at 25°C. show a maximum in the recovery vs. *p*H curve at a *p*H of about 10.5, which corresponds to a calcium hydroxide/aluminum ratio of about 1.5. The rapid drop in recovery as *p*H increases is attributed to formation of an insoluble compound containing calcium and aluminum. The maximum occurs both for $E_1$, which contains only sodium bicarbonate, and for $E_2$, which represents an average composi-

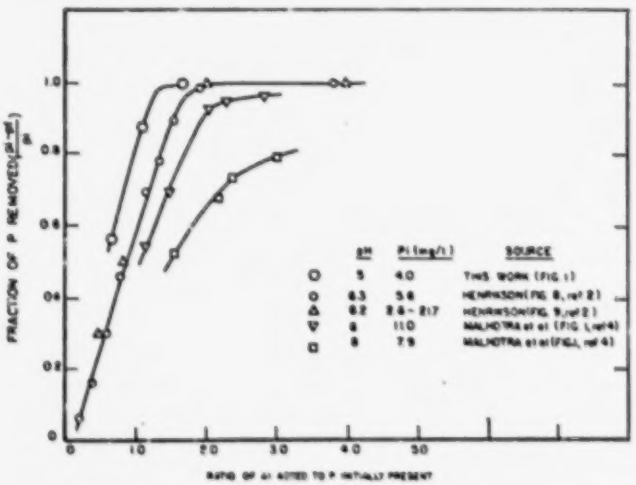

Fig. 5. Comparison of phosphate removal results from various sources.

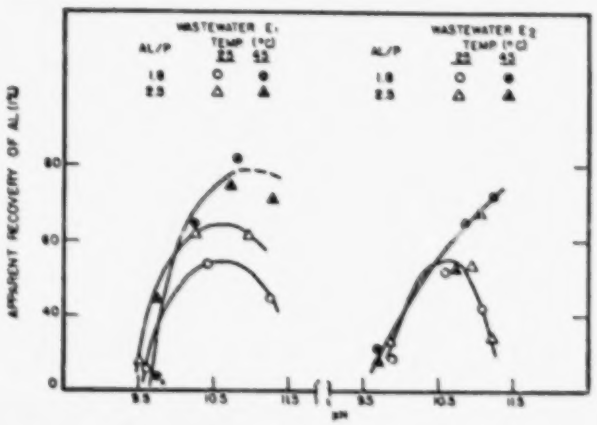

Fig. 6. Influence on aluminum recovery of temperature, aluminum/phosphate ratio, and wastewater type.

tion for a secondary effluent. Wastewater $E_1$ shows better recovery for the higher aluminum/phosphate ratio at 25°C., whereas for wastewater $E_2$ there is no noticeable difference for the two ratios at either temperature. The most striking effect is the high recovery at 45°C. at the high values of *p*H. Indications are that the insoluble calcium-aluminum compound which limits recovery at 25°C. is more soluble at the higher temperature. In all tests, even at 45°C., no phosphate was present in solution.

The difference in recovery with the two synthetic wastewaters prompted studies with actual wastewaters. These tests also provided an opportunity for evaluating the enrichment procedure for producing sludge. Two wastewaters were used in this experiment: secondary effluent from the trickling filter plant at Batavia, Ohio, and from the activated sludge plant at Lebanon, Ohio. The experiment was conducted at 25°C.

Data were obtained for the two wastewaters at three calcium hydroxide/aluminum ratios (1.0, 1.5, 2.0), by using the two sludge production techniques. Tests were carried out at an aluminum concentration of 200 mg./liter. The effect of diluting the reaction mass with distilled water to 100 mg./liter of aluminum was also evaluated.

The data obtained with the two wastewaters are shown in Figure 7. The data for the 200 mg./liter aluminum concentration show the same peaking in recovery at a *p*H of 10.5 (that is, about 1.5 calcium hydroxide/aluminum). The two wastewaters show virtually indistinguishable results under the different conditions. There apparently is an effect of the enrichment procedure in these tests with real effluents. The shape of the recovery vs. *p*H curves are seen to be different, and the recovery is about 10% higher for the sludges prepared by the enrichment procedure, despite a lower aluminum/phosphate ratio in the sludge. Dilution of the reaction mass increased recovery for the more realistically prepared sludge but not for the sludge made by the enrichment procedure. For these wastewaters, maximum aluminum recoveries are seen to be about 45% at 200 mg./liter aluminum if the more realistic sludge preparation procedure is followed.

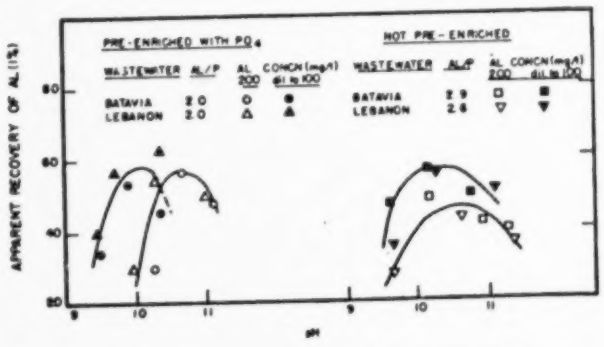


Fig. 7. Influence on aluminum recovery of wastewater type, dosing with phosphate, and dilution after reaction.

## USE OF CALCIUM HYDROXIDE—SODIUM HYDROXIDE MIXTURES

A series of tests were carried out to determine the proper proportions of calcium hydroxide and sodium hydroxide which give the maximum recovery of aluminum. Synthetic wastewater $E_2$, which represents an average effluent, was used, and sludge with an aluminum/phosphate molar ratio of 2 was produced by using the phosphate enrichment technique. Tests were carried out at sodium hydroxide/aluminum molar ratios of 0.5, 1.0, 1.5, 2.0, and 2.5. At each of these ratios, tests were made at the following six values of the calcium hydroxide/aluminum molar ratio: 0, 0.5, 1.0, 1.5, 2.0, and 2.5. A few extra runs were made at sodium hydroxide/aluminum ratios of 3.0, 3.5, and 4.0, with no calcium hydroxide addition. Sodium hydroxide solution and calcium hydroxide slurry were added simultaneously, and agitation was continued for 4 hr. The tests were run at 25°C. and a total aluminum concentration of 200 mg./liter aluminum.

The data obtained in these experiments are presented in Figures 8 and 9, where percent recovery is plotted as a function of *p*H. Lines of constant sodium hydroxide/aluminum ratio are shown in Figure 8. The increases in *p*H on any given curve are the result of successive increases of 0.5 in the calcium hydroxide/aluminum ratio, starting from 0 and progressing to 2.5. At any given sodium hydroxide/aluminum ratio, aluminum recovery increases with increasing *p*H (and calcium hydroxide/aluminum dose) to a maximum at a *p*H of about 11 and then drops sharply. As expected, the curves for higher sodium hydroxide/aluminum ratios show higher aluminum recoveries.

The same data are shown in Figure 9, where lines of constant calcium hydroxide/aluminum ratio are shown.

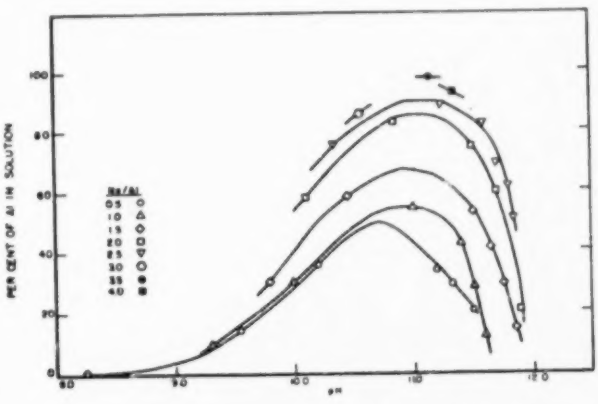


Fig. 8. Solubilization of aluminum oxide-phosphate sludge. Effect of calcium hydroxide at a number of sodium hydroxide/aluminum ratios.

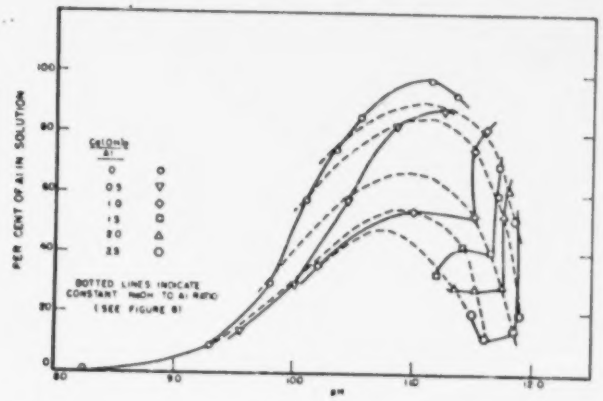


Fig. 9. Solubilization of aluminum oxide-phosphate sludge. Effect of sodium hydroxide at a number of calcium hydroxide ratios.

The lines of constant sodium hydroxide/aluminum ratio shown in the preceding figure are shown dotted. The increases in *p*H on any one of the solid lines are the result of increments of 0.5 sodium hydroxide, aluminum starting at 0.5 and progressing to 2.5. The shape of the curves for calcium hydroxide/aluminum levels of 1.0 and higher is quite unusual. The rapid increase in aluminum recovery with sodium hydroxide addition at no increase in *p*H may be due to suppression of the solution of the calcium hydroxide by the large amount of sodium hydroxide already in the dissolved state.

In the runs in which the calcium hydroxide/aluminum ratio was 0.0 and 0.5, the recovery of aluminum was accompanied by redissolving of phosphate. At the calcium hydroxide/aluminum ratios of 1.0 and higher, no phosphate was found in solution. The important condition for phosphate removal is clearly the calcium/phosphate ratio. Since aluminum/phosphate ratio in the sludge was 2.0, this corresponds to a calcium hydroxide/phosphate ratio of 2.

Conditions for maximum recovery can be determined from Figure 9, with the limitation (for these runs) that calcium hydroxide/aluminum ratio must be 1.0 or greater. Maximum recovery is seen to occur at a calcium hydroxide/aluminum ratio of 1.0 and a sodium hydroxide/aluminum ratio of 2.5. Recovery is 82% at this point. Approximately the same recovery could be obtained at a sodium hydroxide/aluminum ratio of 2.0 if the calcium hydroxide/aluminum ratio were reduced to slightly less than 1.0.

The possibility that aluminum recovery is limited by the presence of an insoluble calcium-aluminum salt was investigated by plotting various ionic products against *p*H. The ionic product, $[Ca]^2[Al]$ gives evidence of a solubility product limitation. In Figure 10, this product is plotted against *p*H for each of the sodium hydroxide/aluminum ratios investigated. In all cases, the ionic

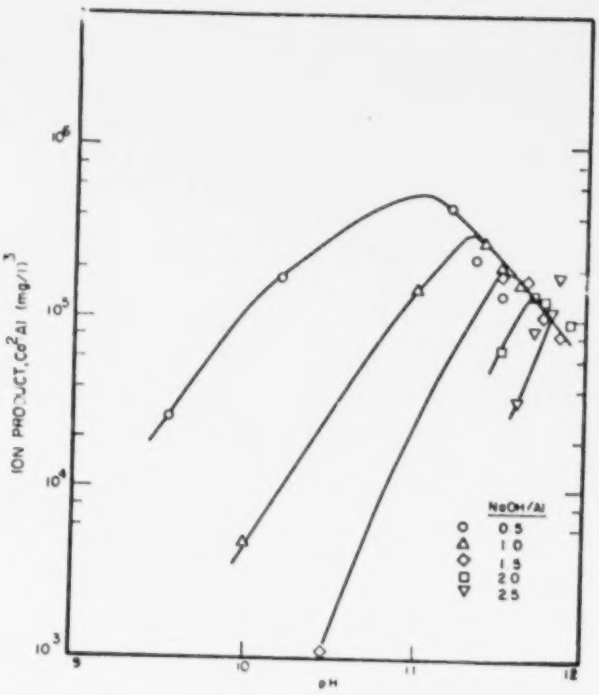


Fig. 10. Ionic product $(Ca)^2(Al)$ for supernatants of calcium hydroxide-sodium hydroxide resolubilization experiment.

product increases until a limiting *p*H is reached. Then all of the curves merge into a common limiting line. The slope of this line is −1, indicating a constant value of the product $[Ca]^2[Al][OH]$. A metastable calcium-aluminum salt with this molar ratio of calcium to aluminum has been suggested by Wells et al (*10*) in an extensive study of the phase relationship of the system calcium-oxide-aluminum oxide-water.

If a limiting solubility product of this nature exists, it indicates that aluminum recovery will be maximized by operating at low calcium concentrations and as low a *p*H as is consistent with the requirement that the aluminum hydroxide-phosphate complex be broken down. The existence of this limiting solubility product must be considered tentative until confirmed by investigations in systems of controlled ionic composition.

## DISCUSSION

### PHOSPHATE REMOVAL

The results of the studies on the effect of aluminum dose on phosphate removal have verified the existence of a *p*H optimum for phosphate removal. The difference in the shape of these curves (Figures 1 and 2) for a synthetic and a real wastewater is significant. The ionic composition and concentration apparently have a strong effect on the influence of *p*H on phosphate removal.

A reconsideration of Slechta and Culp's data has

shown that the poor phosphate removals reported by these authors for alum-sodium aluminate mixtures high in aluminate were most likely the result of the high values of *p*H produced in the wastewater by these mixtures. These *p*H values were too far removed from the optimum *p*H to allow adequate phosphate removal. However, the data of these authors show an optimum *p*H range even narrower than obtained with the synthetic effluent in this work and extending only up to a *p*H of 7. This could be due to the fact that Slechta and Culp did not filter the supernatants before analysis, or possibly to an effect of sulfate which makes alum more effective than sodium aluminate. Stumm and Morgan (9) have discussed the influence of anions on aluminum hydroxide coagulation.

The method of presentation of phosphate removal data used in Figures 4 and 5 in which fractional removal is plotted against the aluminum/phosphate molar ratio is expected to be quite useful in comparing the data of different investigators. The fact that the data correlate well when presented in this fashion lends further credence to the position that the removal of phosphate takes place by means of a chemical reaction rather than by adsorption. With an adsorption mechanism, the relative loading of aluminum to phosphate on the floc would be expected to correlate with the concentration of phosphate remaining in solution. In this correlation, the relative loading correlates with the fraction of phosphate remaining (1-fraction removed = fraction remaining) and not with the concentration remaining in solution. This result is consistent with chemical removal but not with adsorption.

## ALUMINUM RECOVERY

The results of this work indicate that aluminum ion recovery of more than 50% is unlikely for a single-stage treatment process with calcium hydroxide or lime at ambient temperatures. Higher recoveries could doubtlessly be obtained at lower aluminum concentrations than the 200 mg./liter aluminum used in this work. However, lower concentrations of aluminum mean a higher proportion of sludge to be treated to wastewater throughput, with consequent high capital costs. Conducting the reaction at higher temperatures may be much more effective, but the cost of heating sludge could be prohibitive. Preliminary results show aluminum recoveries in the order of 80% at concentrations of aluminum of 400 mg./liter in the sludge, by using calcium hydroxide alone at 80°C. This condition would be economically attractive if a major portion of the heat required to raise the sludge to 80°C. could be recovered.

The use of calcium hydroxide-sodium hydroxide mixtures yields a suitably high recovery of aluminum. Sludge mass would be reduced and the sludge upgraded to a point where it might be a source of phosphate. Chemical requirements are substantially higher than would be expected by the stoichiometric equation [Equation (4)]. A significant part of this chemical demand can be attributed to bringing the *p*H of the wastewater containing the floc from a *p*H of 6.2 to a *p*H of over 11. It is likely that experiments conducted at a higher aluminum concentration than 200 mg./liter aluminum would show a lower consumption of sodium hydroxide.

The indications that aluminum concentration in the supernatant after treating the sludge is limited by a solubility product involving calcium and hydroxide point to ways of increasing yield. For example, calcium ion concentration of *p*H can be reduced in a controlled fashion by addition of sodium carbonate and/or carbon dioxide.

A two-stage recovery process may be a method by which chemical consumption can be reduced. One approach would be to recover approximately 50% of the aluminum in a first stage by treatment of dilute sludge (200 mg./liter aluminum) with lime. In a second stage, the undissolved material would be thickened and treated with sodium hydroxide to complete the solution of aluminum.

## CHEMICAL COSTS OF RECOVERY

A comparison has been made in Table 2 of cost of chemicals consumed in the recovery process. In this table, recovery with calcium hydroxide-sodium hydroxide mixtures (cases 1 and 2), and recovery with calcium hydroxide only (case 3), are compared with the costs of no recovery (case 4). It has been assumed that *p*H adjustment of the wastewater will not be necessary in any of the cases. For cases 1 and 2, sulfuric acid is added to neutralize excess sodium aluminate not neutralized by makeup alum. The recovery processes are seen from Table 2 to be less costly than the no-recovery case. A rough estimate of operating cost (including amortiza-

TABLE 2. EFFECT OF RECOVERY CONDITIONS ON CHEMICAL COST OF PHOSPHATE REMOVAL WITH ALUM*

| Recovery Conditions | Case 1 | Case 2 | Case 3 | Case 4 |
|---|---|---|---|---|
| $Na_2O/Al$ (molar ratio) | 2.5 | 2.0 | 0 | 0 |
| $Ca(OH)_2/Al$ (molar ratio) | 1.0 | 0.8 | 1.5 | 0 |
| Anticipated Recovery (%) | 80 | 80 | 40 | 0 |
| Chemical Costs (¢/1000 gal) | | | | |
| NaOH (at 3.4¢/lb) | 1.7 | 1.4 | 0 | 0 |
| $Ca(OH)_2$ (at 1.0¢/lb) | 0.4 | 0.3 | 0.6 | 0 |
| $H_2SO_4$ (at 2.0¢/lb) | 0.1 | 0.1 | 0 | 0 |
| makeup alum (at 2.4¢/lb) | 0.8 | 0.7 | 2.3 | 0 |
| Total Cost | 3.0 | 2.6 | 2.9 | 3.0 |
| Cost based on P removed (¢/1000 gal/mg/l P) | 0.30 | 0.26 | 0.29 | 0.30 |

*Wastewater containing 10 mg/l P, treated with 193 mg/l alum (2 moles Al/mole P)

tion) for a recovery process is 1.0¢/1,000 gal. for a 10 MGD wastewater plant scale. Total costs for the recovery processes are seen to be approximately the same as for the no-recovery case. The recovery processes are expected to reduce sludge handling problems. Although no quantitative data have yet been obtained, the recovery processes appear to produce a sludge which settles and filters better than the untreated aluminum hydroxide-phosphate sludge.

## RECOMMENDATIONS

Hydroxide methods for recovery of aluminum from aluminum hydroxide-phosphate sludges offer promise, although costs are not as low as was anticipated. Treatment with calcium hydroxide at ambient temperatures appears to offer little, since recovery is low. Use of calcium hydroxide in a two-stage process with sodium hydroxide, or alone at elevated temperatures, offers promise and should be investigated further.

The mixed hydroxide process gives a high aluminum recovery and alters the sludge substantially. The dewatering characteristics of the final sludge must be investigated, and its potential as a chemical feedstock should be evaluated.

This investigation has verified results of other authors concerning pH optima for phosphorous removal, and the ratio of phosphorous removed to aluminum added, and suggests a correlation method which will aid comparison of results of different investigations. Many important questions remain unanswered. The differences between effluents and the effect of filtering after decanting on results are some of the areas where further effort is needed. Other interesting areas for further work are means for increasing the ratio of phosphorous to aluminum in the sludge and cheaper means for introducing the aluminum ion into the wastewater. More study should be carried out on phosphate removal by sodium aluminate, which is the form in which aluminum is returned to the phosphate removal step in hydroxide types of recovery processes.

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